

Report for 2003IL22B: Rapid Solar Transformation of Nutrients in Natural Waters

There are no reported publications resulting from this project.

Report Follows

Problem and Research Objectives - Solar phototransformation of nitrogen nutrients between forms such as organic nitrogen, nitrate, and ammonia can provide significant sources and sinks for the individual nutrient forms. Solar irradiation of natural organic material (NOM) can generate reactive species including free radicals, that can drive transformations such as the generation of ammonia. Recognition of these contributions may impact the setting of water quality standards and best management practices for nutrients, as well as nutrient modeling. The objectives of the project are to 1) measure the photogeneration of ammonia in several Illinois waters, 2) identify important transformation pathways, and 3) derive models for the process rates in terms of water quality parameters, which may be suitable for adaptation into water quality models.

Methodology

Photoammonification rates are being measured in water samples brought to the laboratory, using simulated solar light and standard methods (phenate) for ammonia measurement, as well as other important water quality parameters. Pathways are being identified by two types of experiment: 1) model sensitizers (sources of reactive species) are irradiated in the presence of model ammonia precursors that mimic various nitrogen functional groups known to be present in NOM, in order to determine which combinations lead to ammonia production, and 2) water samples are spiked with sensitizers and (in separate experiments) model precursors, to determine which are present in the waters, and which component (sensitizer or precursor) is the limiting factor in ammonia production. Depending on the results, specific radical "probe" compounds may be used to measure radical production in the waters upon irradiation with simulated sunlight in several spectral regions. This information will be compared for various waters, and, along with the solar emission and water absorbance spectra can be used to predict ammonia photoproduction. We will also attempt to develop simple mechanistic/kinetic models of the processes for use in predictive purposes.

Principal Findings and Significance

Work this year has been focused in two areas: 1) Measurement of the amount of ammonia produced photochemically from various natural waters upon irradiation with UV/visible light, and 2) determination of the reactive species and nitrogen functional groups that serve as ammonia precursors, in order to elucidate the major pathways by which ammonia is photochemically produced from natural organic material (NOM).

Photochemical Ammonia Production in Natural Waters -

Samples of several natural waters have been collected and returned to the laboratory for use in photochemical experiments. Although a variety of samples is being used, the majority of work has been focused on three local waters because of their differences and similarity, their ready availability, and interest in the variability throughout the year. For best consistency and comparability of measured values, a UV/visible lamp is used for irradiation of samples in the laboratory, and the results extrapolated to those of solar irradiation by calculation using spectra of the lamp emission, solar spectrum, and absorbance spectra of pyrex reactors, waters, and model compounds. Filtered and microfiltered (0.2 μm) waters were irradiated and ammonia formation monitored. Ammonia increases of 10% to 400% have been observed upon irradiation, implying that the amount of ammonia measured in some environmental samples may depend significantly on previous sunlight exposure, as transport phenomena such as nitrogen spiraling should be impacted. The initial ammonia concentration, extent of production, and evolution curve all change throughout the year, as well as with sample storage, even at 4° C after microfiltration.

The curve shape for ammonia evolution can provide information about the process. In its simplest form, ammonia production requires a photosensitizer, which upon irradiation produces a transient species that reacts with an ammonia precursor (a nitrogen-containing functional group in the NOM) to produce ammonia. If both sensitizer and precursor are present, ammonia production should begin immediately and the rate gradually slow until a plateau is reached. A plateau in ammonia production indicates that sensitizer and/or precursor has been exhausted. The rate and extent of the reaction should be dependent upon the nature and amount of sensitizer and precursor. A delay in ammonia production indicates that sensitizer and/or precursor must be

produced in a prior step before they can generate ammonia in a secondary step. Although the relationship between season and curve shape is not obvious for the 29 photoammonification experiments on local waters to date, 67% of the water samples collected during the summer (June-August, 6 samples) showed a lag phase in ammonia production, compared to only 29% in April-May (17 samples) and 17% of fall samples (Sept-Oct, 6 samples). Twenty-three of the 29 samples reached a plateau in ammonia production within 1-3 hours. Curve analysis is ongoing.

Mechanisms of Ammonia Photoproduction -

Much is known about the photoproduction of reactive species (RS), the types of compounds with which they react, and the products that are formed. In order to determine the functional groups responsible for ammonia production from NOM, RS reported or hypothesized to be produced photochemically from NOM were identified, along with the important (i.e., most plentiful) nitrogen-containing functional groups in NOM. The RS produced by these sensitizers, and model compounds (MC) representing the important nitrogen-containing functional groups were used in screening experiments to identify RS-precursor combinations that were capable of producing ammonia. RS identified included 1) free radicals such as hydroxyl, peroxy, carbonate radical, and carbon-centered radicals formed by oxidation of an organic compound by another oxidizing radical, 2) triplet states from aryl ketones such as benzophenone, 3) excited states of quinones and their corresponding semiquinone radicals, and 3) other excited species such as singlet oxygen. Carbon-centered radicals quickly react with oxygen to form peroxy radicals at the oxygen concentrations present in surface water. Peroxy radicals fall into two classes, oxidizing and reducing, but the reducing radicals quickly eliminate superoxide. Superoxide is a special case, as it can both oxidize and reduce, reducing triplet aryl ketones and quinones to ketyl radicals and semiquinones, respectively, and Fe(III) to Fe(II). Among the oxidizing radicals hydroxyl, peroxy (including superoxide), carbonate, etc., hydroxyl is the strongest, and was used for screening on the premise that if a precursor did not react with hydroxyl, it would not be oxidized by a weaker radical. Benzophenone and benzoquinone were selected to be representative of the aryl ketone and quinone classes, partly because of the wealth of data on their photoreactions. Singlet oxygen was shown by competition calculation to essentially be completely quenched by water. The above reasoning reduced the number of radicals used in the screening tests to those shown as column labels along the top of the table shown below.

Nitrogen-containing functional groups thought to be plentiful in NOM included amines, amides, and pyridine functionalities. Amino acids and amino alcohols are included in the amine category, and peptides and ureas fall into the amide category. These candidate precursor groups and their representative MCs are listed along the left-hand side of the table as row labels. In addition to RS-MC experiments to determine feasibility of the combinations, sensitizers or model precursors were added to various natural waters for irradiation, to determine which types of sensitizers and/or precursors are present in the NOM, and whether sensitizer or precursor was the limiting factor in ammonia production.

Results obtained to date are shown in the table, where + and ++ denote possible and definite ammonia production in RS-MC compound experiments or enhancement of ammonia production in RS- or MC-amended natural waters. A minus sign indicates that no effect was observed. Hydroxyl radical has been shown to generate ammonia when reacting with amines, or with the NOM in, or isolated from, surface water. A trace amount of ammonia was produced by the attack of OH radical on acetamide, but a yield of only 5% was observed based on the amount of acetamide destroyed, because of a very unreactive intermediate that is formed. In the reaction of hydroxyl radical with diethylamine on the other hand, ammonia production is almost quantitative. The benzophenone triplet excited state also produced ammonia when benzophenone was irradiated in natural waters or solutions of reconstituted Suwannee River Humic Acid (SRHA), but did not produce ammonia from acetamide in pure water. Irradiation of benzoquinone produced ammonia from SRHA but not from Salt Fork River water. These last two results are tentative, pending replication. No experiments have yet been performed using the pyridine model compound nicotinic acid.

Reactive Species or Precursor class		Oxidizing Radical	Aryl Ketone Triplet	Quinone Triplet	NOM
Representative Substance		OH radical ⁽¹⁾ (H ₂ O ₂ /UV, nitrate)	benzophenone	benzoquinone	Homer L., Collins P., Salt Fork R., SRHA
Amine	diethylamine ethylamine	++ ++ ++ ⁽²⁾			
Amide	acetamide	(-)			
Pyridine	nicotinic acid				
NOM	Homer Lake Collins Pond Salt Fork R. Clinton Lake SRHA	++ ++ ++	++ ++	 (-) (+)?	++ ++ ++ ++ ++

Notes:

1) generated by either H₂O₂ or nitrate photolysis.

2) trace amount found – only 5% based on acetamide consumed.